EFFECTS OF CATALYST ACIDITY AND STRUCTURE ON POLYMER CRACKING MECHANISMS

Rong Lin, Darrel L. Negelein, and Robert L. White
Department of Chemistry and Biochemistry
University of Oklahoma, Norman, OK 73019

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INTRODUCTION

Communities in the United States need alternatives to municipal solid waste landfilling. Of the solid waste components currently placed into landfills, plastics are particularly undesirable because of their limited biodegradability. A variety of plastic waste recycling methods have been established and new recycling approaches are being developed to avoid placing polymers into landfills. One approach to waste plastic recycling, known as tertiary recycling, consists of converting plastics into useful chemicals. The development of efficient processes for waste plastic tertiary recycling will require detailed fundamental data on the direct catalytic cracking of polymers without complications due to reactions of primary cracking products with polymer residue. Secondary reactions can be minimized by maintaining high catalyst to polymer ratios and providing efficient and rapid removal of volatile products. This work was carried out to investigate the potential use of catalytic cracking to convert plastics wastes into mixtures of useful chemicals. The effects of silica-alumina, HZSM-5 zeolite and sulfated zirconia catalysts on the thermal degradations of poly(ethylene), poly(propylene) and poly(styrene) are described.

EXPERIMENTAL

Samples examined in this study were: poly(ethylene) (PE) (MW=80,300), poly(propylene) (PP) (MW= 250,000), poly(styrene) (PS) (MW=850,000), and these polymers coated on silica-alumina, HZSM-5, and sulfated zirconia cracking catalysts (10-20% (wt/wt)). All polymer samples were purchased from Aldrich Chemical Company (Milwaukee, WI). The silica-alumina catalyst was provided by Condea Chemie GmbH (Hambug, Germany) and contained 11.8% by weight alumina and had a surface area of 282 m^2/g. The HZSM-5 zeolite was obtained from Mobil Oil (Paulsboro, NJ) and was characterized by a 1.5% alumina content and a 355 m^2/g surface area. The sulfated zirconia catalyst was synthesized by following procedures described previously[1]. The sulfated zirconia catalyst had a surface area of 157 m^2/g and contained 9% by weight sulfate. Polymer/catalyst samples were prepared by dissolving polymers in proper solvents, adding catalyst, and then rotoevaporating the mixture to remove solvents. The resulting PE and PP coated catalyst samples were dried at 120°C, and the PS coated catalyst samples were dried at 90°C for several hours.

The apparatus used for pyrolysis-GC/MS, TG-MS and TG-GC/MS measurements have been described previously[2,3]. Pyrolysis separations were achieved by using a HP 5890 capillary GC with a DB-5 column (0.25 μm film thickness). The gas chromatograph oven temperature program consisted of a 2 min isothermal period at -50°C followed by a 5°C/min ramp to 40°C followed by a 10°C/min ramp to 280°C, and then isothermal at 280°C for 5 minutes for PE and PP samples. For PS samples, the GC oven temperature programs consisted of a 2 minute isothermal period at -50°C followed by a 10°C/min ramp to 280°C, and then another isothermal period at 280°C for 5 minutes. For TG-MS studies, samples were heated from 50°C to 600°C at nominal heating rates of 1, 10, 25, and 50°C/min, with a He purge gas flow rate of 50 mL/min. For TG-GC/MS studies, a Valco Instruments, Inc. (Houston, TX) eight port heated sample injector was employed to divert small volumes (ca. 100 μL) of TG effluent into a 30 m DB-5 capillary column (0.25 μm film thickness). TG-GC/MS signal averaged mass spectra were acquired at rates ranging from one to two per second, depending on the mass range that was scanned. A 5 mL/min He carrier gas flow rate through the TG-GC/MS chromatographic column was employed for all separations. TG-GC/MS column effluent was split prior to entering the mass spectrometer to maintain an ion source pressure of 5×10^{-5} torr.

RESULTS AND DISCUSSION

Figure 1 shows pyrolysis GC/MS results for neat PE and PE/catalyst samples obtained at 500 °C and demonstrates the dramatic effects of catalysts on PE thermal degradation[4]. All four chromatograms shown in Figure 1 were obtained by using the same separation conditions and they are plotted on the same time scale. The bottom chromatogram represents the volatile products from pyrolysis of neat PE at 500°C and contains numerous high molecular weight species. However, in the presence of cracking catalysts, more than 85% of volatile products were hydrocarbons in the C_2 to C_{10} range. Therefore, the effect of the catalyst was to restrict the molecular weight range of volatile products, leading to the formation of low molecular weight species. With increasing catalyst acidity, more saturated hydrocarbons were produced relative to unsaturated hydrocarbons. Large amounts of aromatics were detected for the sample containing HZSM-5 zeolite. The most abundant volatile products generated by PE cracking were isoalkenes, which differs from previous reports that isoalkanes were the primary products. However, the mechanisms proposed for isoalkane formation require protonation of initially formed alkenes followed by hydride abstraction from the polymer residue. The rapid removal of volatile products during cracking minimized secondary reactions and therefore was an effective means to study the effects of catalysts on the initial polymer cracking reactions. TG-MS results indicated that poly(ethylene) cracking on all three catalysts occurred in three steps. Saturated and unsaturated hydrocarbons evolved in the first two steps and aromatics evolved in the third step.

Pyrolysis GC/MS results for neat PP and PP/catalyst samples obtained at 500 °C are shown in Figure 2. The presence of catalysts led to the preferred formation of low molecular weight species. Volatile product distributions depended on the choice of catalyst[5]. It was found that the most abundant neat PP thermal degradation volatile products were C_3 to C_{15} olefin homologues separated by three carbon atom intervals. The most abundant saturated volatile products were C_5 alkanes. Catalytic cracking of PP/SA samples produced a significantly different volatile product distribution than neat PP thermal degradation. The most abundant volatile products were C_4, C_5 and C_6 alkenes. The amount of char remaining on catalyst surfaces was found to be approximately 1% of the initial polymer mass. In the presence of ZrO_2/SO_4 catalyst, the most abundant volatile products were saturated hydrocarbons. All of the volatile products detected were C_{10} or smaller. However, an increase in unsaturated volatile product yields was found at higher temperature. The significant difference between PP/Si-Al and PP/ZrO_2/SO_4 cracking products indicates that catalyst acidity plays a vital role in determining volatile product slates. Sulfated zirconia, a very strong acid catalyst, significantly lowered the temperature at which catalytic cracking occurred and facilitated hydride abstractions, resulting in large yields of saturated hydrocarbons and the formation of large amounts of residue (ca. 15%). Like the PP/Si-Al sample, the PP/HZSM-5 sample yielded primarily unsaturated volatile products. The organic residue left on catalysts was estimated to be approximately 1%. In contrast to the PP/Si-Al and PP/ZrO_2/SO_4 samples, HZSM-5 channels restricted reaction volume, which resulted in relatively large yields of alkyl aromatics.

Catalytic cracking mechanisms of PS also differ considerably from the thermal degradation mechanisms[6]. Pyrolysis GC/MS results (Figure 3) indicate that styrene was the most abundant volatile product resulting from neat PS thermal degradation. The relative yield of styrene was 68% when PS was pyrolyzed at 400 °C. However, benzene was the most abundant product when PS was catalytically cracked. The relative yield of benzene was found to be as high as 60% for the PS/HZSM-5 sample and over 30% for samples containing Si-Al and sulfated zirconia catalysts. Very little styrene was detected for all three PS/catalyst samples. TG-GC/MS results for the PS/ZrO_2/SO_4 sample are shown in Figure 4. The broken line in this figure denotes the TG weight loss curve for the sample. Polymer decomposition occurred primarily between 150 and 350 °C. The second weight loss step results from the decomposition of the catalyst. The solid line in Figure 4 denotes the TG-GC/MS total ion current, which is plotted as a function of the TG temperature at which GC injections were made. This plot contains 31 separate chromatograms obtained during one TG weight loss analysis. It can be seen that at low temperature there is only one peak, corresponding to benzene. With the increasing of temperature, more peaks appear in chromatograms, indicating the formation of more cracking products. Peaks at high temperature (i.e > 400 °C) correspond to the formation of SO_2 and suggest that the sulfated zirconia catalyst decomposed. Figure 5 shows a TG-GC/MS chromatogram obtained from TG effluent that was injected when the TG sample temperature was 240 °C. More than 25 peaks were detected in this chromatogram. The broken line in Figure 5 denotes the GC oven temperature ramp employed for separations. It was found that benzene was by far the most abundant volatile product and was produced at temperatures well below those at which the other volatile products were detected. All of the PS/catalyst samples produced alkyl benzenes and indanes, but styrene and indenes were only detected for samples containing HZSM-5 zeolite.

TG analyses were carried out to investigate the effects of catalysts on volatilization activation energies. TG weight loss data obtained by using different heating rates (1, 10, 25 and 50 °C/min) were used to calculate volatilization activation energies by using the method described by Friedman[7]. Volatilization activation energies calculated from TG weight loss information are given in Table 1. The highest volatilization activation energies were obtained for the neat polymer samples. All three catalysts lowered the activation energy for PE thermal degradation significantly. The order of catalyst activities was found to be in the order of increasing catalyst acidity: ZrO_2/SO_4 > HZSM-5 > Si-Al.

CONCLUSIONS

The effects of different catalysts on catalytic cracking product distributions derived from polymer/catalyst samples were studied. It was found that volatile product distributions were affected by the choice of catalyst as well as the cracking conditions. In general, catalysts caused volatile hydrocarbon products to be smaller than neat polymer thermal decomposition products. Overall volatilization activation energies for PE, PP, and PS thermal decompositions were considerably reduced by the presence of cracking catalysts and the magnitude of the reduction depended directly on the catalyst acidity. A lowering of the overall volatilization activation energies by cracking catalysts is desired for polymer recycling applications because it greatly reduces the cracking temperature required to decompose plastic wastes, which, reduces operational costs of the process.

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Table 1. Volatilization Activation Energies (kcal/mol)

Catalyst	PE	PP	PS
none	59 ± 1	48 ± 1	49 ± 1
Si-Al	37 ± 3	33 ± 1	39 ± 1
HZSM-5	31 ± 1	29 ± 1	36 ± 1
ZrO_2/SO_4	28 ± 2	27 ± 1	29 ± 2

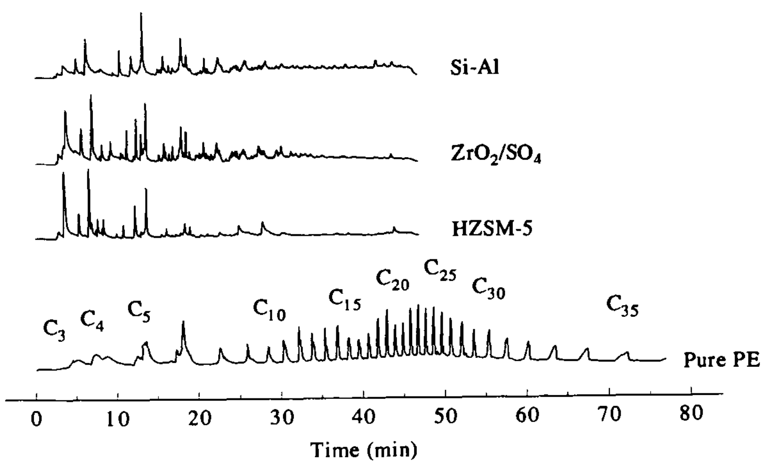

Figure 1 - 500 °C pyrolysis GC/MS chromatograms for poly(ethylene) samples.

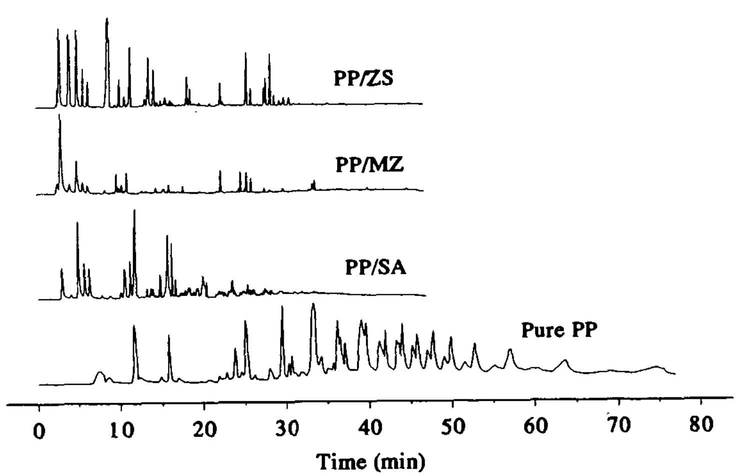

Figure 2 - 500 °C pyrolysis GC/MS chromatograms for poly(propylene) samples.

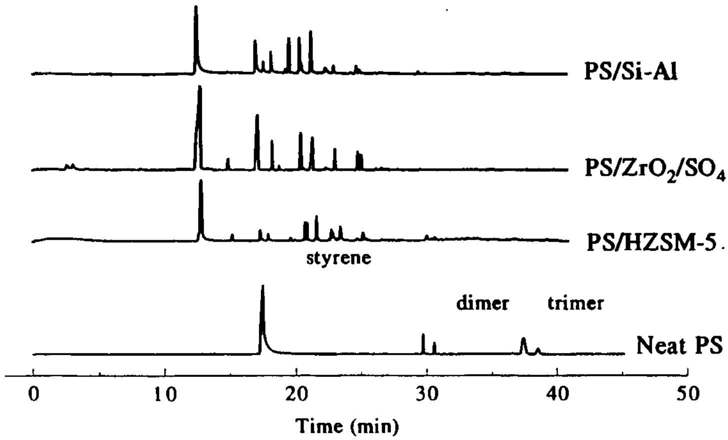

Figure 3 - 400 °C pyrolysis GC/MS chromatograms for poly(styrene) samples.

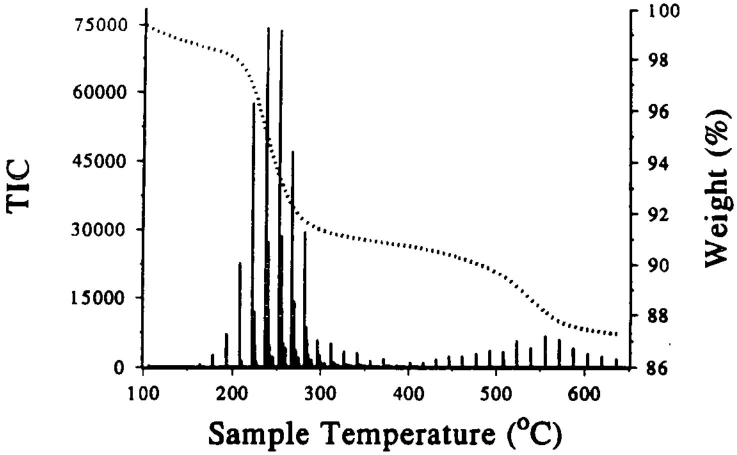

Figure 4 - TG-GC/MS weight loss curve (dotted line) and chromatograms (solid line) for the $PS/ZrO_2/SO_4$ sample.

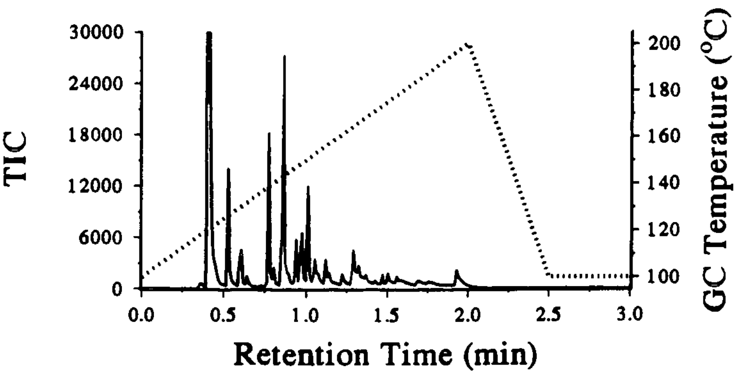

Figure 5 - TG-GC/MS chromatogram measured at 240 °C.